



Europäisches Patentamt  
European Patent Office  
Office européen des brevets

Publication number:

0 005 998  
A1

## EUROPEAN PATENT APPLICATION

Application number: 79300993.7

Int. Cl.<sup>2</sup>: C 07 C 53/02  
C 07 C 51/09

Date of filing: 30.05.79

Priority: 05.06.78 US 912189

Date of publication of application:  
12.12.79 Bulletin 79/25

Designated Contracting States:  
AT BE CH DE FR GB IT LU NL SE

Applicant: Leonard, Jackson Day  
7002 Boulevard East  
Guttenberg New Jersey, 07093(US)

Inventor: Leonard, Jackson Day  
7002 Boulevard East  
Guttenberg New Jersey, 07093(US)

Representative: Allam, Peter Clerk et al.  
TREGEAR, THIEMANN & BLEACH Enterprise House  
Isambard Brunel Road  
Portsmouth, Hants PO1 2AN(GB)

Preparation of formic acid by hydrolysis of methyl formate.

The invention provides a process for the preparation of formic acid by hydrolyzing methyl formate with water at high temperature and pressure in the presence of a formic acid catalyst. Methanol is also formed. The reesterification of the reaction products to methyl formate (a reaction favored by high temperatures) is minimized by flashing the reaction product at relatively low pressure and temperature and thereafter distilling the residual liquid. This procedure separates the methyl alcohol from the formic acid with a minimum contact time and at a low temperature which does not favor the reesterification reaction. High purity formic acid may be obtained by subjecting the bottom from the vacuum distillation of further distillation.

In a preferred embodiment of the invention, prior to the main hydrolysis, the methyl formate is partially hydrolyzed to form the small amount of formic acid needed to accelerate the main hydrolysis step. Accordingly, the necessary formic acid catalyst is formed *in situ*, thus eliminating the need to add formic acid or to recycle product formic acid.

TITLE: PREPARATION OF FORMIC ACID BY HYDROLYSIS OF  
METHYL FORMATE

The formation of formic acid by the hydrolysis  
5 of alkyl formates is well-known in the art. The major  
drawback of such processes from the commercial stand-  
point is that the chemical equilibrium of the hydrolysis  
reaction does not favor the rapid formation of  
substantial amounts of formic acid. Even with  
10 mineral acid catalyst and high temperatures, the  
extended residence time necessary to reach equilibrium  
makes the process very complicated and expensive.  
Examples of such processes are shown in U.S. Patent  
2,160,064 and British Patent 628,656. Though the  
15 use of the mineral acid catalyst did reduce reaction  
time, it created problems because of its tendency  
to promote the decomposition of the formic acid to  
carbon monoxide and water.

In recent years, the trend has been to perform  
20 the hydrolysis by using formic acid itself as the  
catalyst. While this overcame certain of the decompos-  
ition problems caused by the use of a strong mineral  
acid, the formic acid is less effective in accelerating  
the reaction.

25 To overcome this problem, U.S. Patent 3,907,884  
proposed the use of a solvent system to reduce the  
reaction equilibrium time at temperatures from 25 to  
150°C. This process, however, while it serves to  
increase the reaction rate, is not fully effective  
30 because the reactants during purification tend to  
undergo a reverse reaction, that is, the formic acid  
and the methyl alcohol present in high concentrations

and at high temperatures reesterified to reform substantial quantities to the methyl formate.

Another deficiency with the process taught in U.S. Patent 3,907,884 is that it proposes adding the formic acid catalyst from an extraneous source. Obviously, this procedure results in decreasing the net production of formic acid and effectively reducing the capacity of the equipment.

10       The subject invention concerns a process for obtaining improved yields of formic acid by the hydrolysis of methyl formate in the presence of formic acid catalyst. In the process the hydrolysis is carried out at an elevated temperature and pressure using a molar excess of the methyl formate. The reaction products, after equilibrium is reached, are passed to a low pressure zone wherein a substantial quantity of the unreacted methyl formate is instantaneously flashed overhead. The liquid in the flash zone is thereby quickly cooled and then passed directly to a distillation zone, whereby the methyl alcohol and residual methyl formate are rapidly separated from the formic acid-water residue.

25       Because the formic acid and the methanol formed in the reaction are in contact only briefly at a reduced temperature and because the methyl formate concentration is high during their contact, reesterification is almost negligible.

30       Additionally, in a preferred embodiment of the invention, methyl formate and water are introduced into a preliminary hydrolysis zone maintained at an elevated temperature and pressure. In this reactor,

though no formic acid is added, the methyl formate is partially hydrolyzed to form sufficient formic acid to catalyze the main hydrolysis step. The  
5 partially hydrolyzed product from this preliminary step is combined with the recycled methyl formate and water so that the total feed to the main hydrolysis contains a molar excess of the methyl formate.

As already indicated, the present invention  
10 relates to the preparation of formic acid by the hydrolysis of the methyl formate in the presence of a formic acid catalyst. More specifically, the invention relates to a high pressure-high temperature continuous reaction autocatalyzed by formic acid, where-  
15 by the reaction product is processed so as to substantially eliminate the reesterification of the reaction products during purification. Reesterification is further suppressed by using a molar excess of methyl formate in the hydrolysis.

20 The formic acid catalyst required for the main hydrolysis can be added to the reaction zone, as by recycling product formic acid in a continuous process, but preferably is formed in a preliminary hydrolysis zone wherein methyl formate and a  
25 mixture of steam and water are introduced into a high temperature-high pressure zone. The main hydrolysis step of the instant invention is performed at a temperature 90 to 140°C. at pressures from 5 to 18 atmospheres, in the liquid phase at a methyl  
30 formate-water molar ratio of from 1.5:1 to 10:1, preferably from 2:1 to 4:1. Under these conditions the reactants are in a single phase. This eliminates the necessity of employing a solvent system as

proposed by U.S. Patent 3,907,884. While methyl alcohol may be present because of its formation in the hydrolysis the addition of a solvent is not  
5 beneficial to the instant process. A molar excess of the methyl formate drives the reaction in the desired direction.

The products from the main hydrolysis reactor are passed directly to a low pressure zone  
10 which typically is maintained at a pressure of from about 2 atmospheres to 700 mm. Hg, preferably at atmospheric pressure. This zone serves to rapidly cool the products of reaction and reduce the quantities of material which need be subject  
15 to distillation. The liquid from the low pressure zone is fed directly into a distillation zone, preferably in the form of a vacuum distillation column, wherein the methyl alcohol, as well as residual methyl formate, is rapidly separated from  
20 the formic acid and water. Naturally, once the methyl alcohol and the formic acid are separated the reesterification cannot occur. On the other hand, without the low pressure flashing step, the residence time required in the vacuum distillation  
25 would have to be substantially longer, since considerably more material would have to be distilled in the packed column. This flashing procedure also permits the economical operation of the hydrolysis reactor with a stoichiometric excess of the methyl  
30 formate (a condition which improves the amount of formic acid produced and minimizes reesterification) without over-loading the distillation capacity of

the system. In the flashing step a substantial amount of the unreacted methyl formate is vaporized and separated, i.e., at least 25%, preferably at least 50% of the total leaving the main hydrolyzer. The bottom from the distillation zone i.e. primarily water and formic acid may be further distilled for the removal of water and to obtain high purity, e.g. 85%, formic acid.

10 In the embodiment of the invention wherein the formic acid catalyst is generated in situ, prior to the main hydrolysis a portion of the methyl formate and a steam-water mixture is fed to a preliminary hydrolysis reactor maintained at elevated  
15 temperatures and pressure. This reactor is operated at similar conditions to the main hydrolyzer, namely, at temperatures of from 90 to 140°C. and pressures from 5 to 18 atmospheres. Generally lower pressures may be used because of the lower volatility of  
20 the reactants. The methyl formate-water molar ratio is from 0.5:1 to 3:1. Though no formic acid is added to the preliminary hydrolyzer, sufficient hydrolysis takes place to form sufficient formic acid to catalyze the main hydrolysis reaction. In  
25 this latter reaction zone, the contents from the preliminary reactor are combined with the methyl formate and water recycled from the distillation zone. This embodiment is of significant economic advantage because it eliminates the need for  
30 recycling purified formic acid or the addition of extraneous formic acid to the process. Since the preliminary hydrolyzer is an inexpensive addition to the overall process, this technique of forming

the necessary formic acid for catalysis is particularly advantageous. In this embodiment of the invention the recycle methyl formate may constitute  
5 from 60 to 95% of the methyl formate added to the main hydrolyzer, preferably 75 to 90%.

An example of the process of the invention will now be given and reference will be made to the accompanying drawing which schematically illustrates  
10 apparatus for the continuous production of formic acid in large quantities, e.g. 10,000 metric tons per year. The quantities given are pounds per hour but for simplicity only "parts" will be referred to.

Via lines 2 and 3, 3078 parts of methyl formate  
15 and 1340 parts of steam and water are fed to the preliminary hydrolyzer 1. The preliminary hydrolyzer 1 is a glass-lined pipe reactor maintained at a pressure of 10 atm. and a temperature of 120°C. This represents a molar ratio of methyl formate to water  
20 of about 0.7:1.

In the preliminary hydrolyzer 1,460 parts of formic acid, 320 parts of methanol and the 1160 parts of water are formed. About 2478 parts of methyl formate remain unreacted. The effluent is fed via  
25 line 4 into the main hydrolyzer 5 along with the recycle streams 6, 7 and 8. These have the following compositions:

-7-

<u>LINE NO.</u>	<u>METHYL FORMATE</u>	<u>WATER</u>	<u>FORMIC ACID</u>	<u>METHYL ALCOHOL</u>
4	2478	1160	460	320
6	6088	62	285	372
7	10028	-	-	-
8	-	1118	-	-
<u>TOTAL</u>	<u>18504</u>	<u>2340</u>	<u>745</u>	<u>695</u>

The total feed to the main hydrolyzer 5 has a methyl formate/water mol ratio of 2.4:1. This reactor is maintained at a temperature of 120°C. and a pressure of about 9 atm. As will be understood by those skilled in the art, the formic acid formed in the preliminary hydrolyzer 1 serves as a catalyst for the reaction in the main hydrolyzer 5. Because of the severe conditions of temperature and pressure the hydrolysis reaction achieves 95% equilibrium in approximately 20 seconds.

The reaction product from the main hydrolyzer 5 contains 2645 parts of formic acid, 2013 parts of methyl alcohol, 16,116 parts of methyl formate and 1597 parts of water, and passes via line 9 to flash vessel 10. The latter is maintained at atmospheric pressure. In the flash vessel 10 a substantial portion of the unreacted methyl formate, namely 6088 parts, flashes off via line 6 rapidly cooling the remaining liquid. The vapor is recycled to the main hydrolyzer 5. The liquid passes via line 11 to a first distillation column 12, a glass-lined steel column packed with woven glass mats containing only sufficient volume to minimize liquids hold-up. The distillation column 12 is maintained at 400 mm Hg.



pressure and at a bottoms temperature of about 80°C. The temperature of the distillate leaving the column is approximately 22°C and the reflux ratio about 0.6 to 1. The flashing off of the substantial amount of methyl formate in the flash vessel 10 permits the operation of the distillation column 12 at low reflux, at a reduced temperature and with a minimum of contact time. Accordingly, there is negligible reesterification, i.e., less than 0.1%, of the formic acid and methanol reacts. In contrast, if the flashing step is eliminated about 20% of the formic acid fed to the first distillation column reesterifies. Additionally, the low temperature minimizes corrosion problems.

The distillate from the column 12, containing 10,028 parts of methyl formate and 1641 parts of methyl alcohol, passes via line 13 to the second distillation column 14. This column 14 operates at 1.7 atm., a bottoms temperature of about 77°C. and a distillate temperature of 50°C. It is also glass-lined and packed with glass mats. Substantially pure methanol (1641 parts) is taken off as the residue and sent to storage via line 15. The overhead methyl formate is recycled via line 7 to the main hydrolyzer 5.

The residue, 2360 parts of formic acid and 1535 parts of water, from the first column 12 is fed to a third glass-lined distillation column 16 via line 17. The third distillation column 16 is packed with glass mats and operated at about 2.6 atms., a bottom temperature of 142°C, and a

-9-

distillate temperature of  $131^{\circ}\text{C}$ . is maintained.

The overhead stream, consisting essentially of water, is recycled via line 8 to the main hydrolyzer

- 5 5. The residue is removed via line 18, and consists of 2360 parts of formic acid and 417 parts of water, i.e., 85% formic acid.

10

15

20

25

30

## CLAIMS:

1. A process for the preparation of formic acid by the liquid phase hydrolysis of methyl formate in the presence of formic acid as catalyst, which is characterized by the steps of: passing methyl formate and water to a reaction zone maintained at a pressure of from 5 to 18 atms. and a temperature of 90 to 140°C., the molar ratio of said methyl formate to water being from 1.5:1 to 10:1; providing sufficient volume to allow the hydrolysis to approach at least 95% of equilibrium; discharging the resultant product into a low pressure zone, wherein a substantial quantity of the unreacted methyl formate is vaporized overhead and the remaining liquid is thereby quickly cooled; feeding the liquid from said low pressure zone to a distillation zone maintained at a pressure of from 10 to 700 mm. Hg.; and separating the residual unreacted methyl formate and methyl alcohol as a distillate from said distillation zone and a water-formic acid stream as a residue from said distillation zone.

2. A process according to Claim 1, wherein the low pressure zone is maintained at about atmospheric pressure.

3. A process according to Claim 1 or Claim 2, wherein said distillation zone is a vacuum distillation column.

4. A process for the preparation of formic acid by the liquid phase hydrolysis of methyl formate in the presence of formic acid as catalyst, which is characterized by the steps of: passing methyl formate, water and steam to a preliminary hydrolyzer maintained at a pressure from 5 to 18 atms. and a temperature of from

-2-

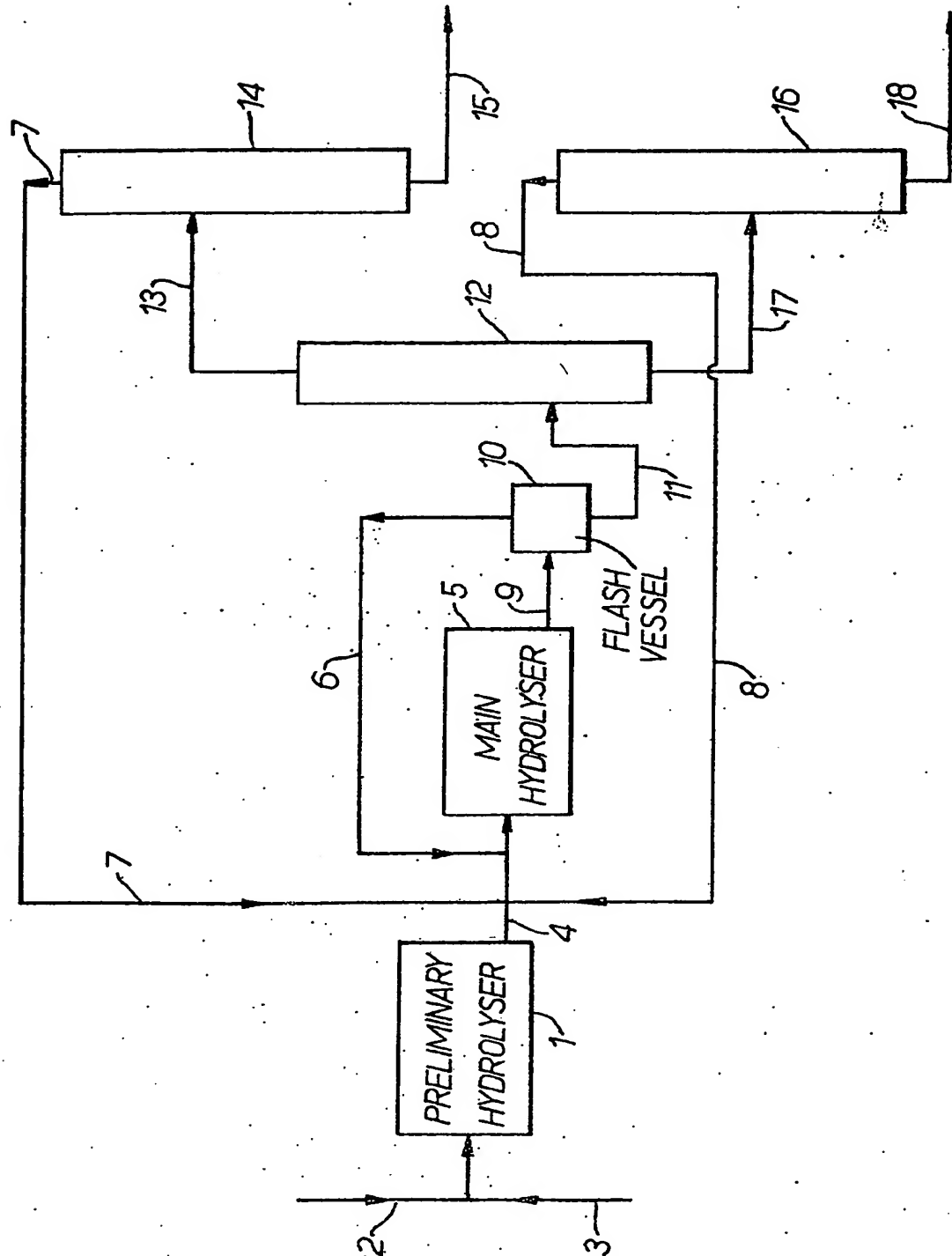
90 to 140°C., the molar ratio of methyl formate and water in said preliminary hydrolyzer being from 0.5:1 to 3:1; partially hydrolyzing the methyl formate to form catalytic quantities of formic acid; passing the effluent directly to a main hydrolyzer; adding to said main hydrolyzer additional methyl formate and water so that the methyl formate-water molar ratio to the main hydrolyzer is from 1.5:1 to 10:1; maintaining said second reaction zone at a pressure of from 5 to 18 atms. and a temperature of from 90 to 140°C.; further hydrolyzing said methyl formate until equilibrium conditions are approached; separating the formic acid, methyl alcohol, unreacted methyl formate and water from said second reaction zone; and recycling of the separated unreacted methyl formate and water to said preliminary hydrolyzer.

5. A process according to Claim 4, wherein the effluent from the second reaction zone is passed to a low pressure zone, wherein a substantial amount of the unreacted methyl formate is vaporized overhead and the remaining liquid is thereby quickly cooled and wherein the liquid from said low pressure zone is subject to distillation to separate the residual methyl formate, the methyl alcohol and the product formic acid.

6. A process according to Claim 5, wherein the low pressure zone is maintained at about atmospheric pressure.

7. A process according to Claim 5 or Claim 6, wherein said distillation is effected in a vacuum distillation column.

TREGEAR, THIEMANN & BLEACH.  
CHARTERED PATENT AGENTS.  
ENTERPRISE HOUSE,  
ISAMBARD BRUNEL ROAD,  
PORTSMOUTH PO1 2AN  
AND  
49/51, BEDFORD ROW, LONDON. WCV 6RL





European Patent  
Office

# EUROPEAN SEARCH REPORT

0005998

Application number

EP 79 300 993.7

DOCUMENTS CONSIDERED TO BE RELEVANT			CLASSIFICATION OF THE APPLICATION (Int. Cl.)
Category	Citation of document, with indication, where appropriate, of relevant passages	Relevant to claim	
A, D	DE - B - 1 035 637 (DEGUSSA) * claim 1; column 3, lines 11 to 14 *	1, 2,6	C 07 C 53/02 C 07 C 51/09
	US - A - 2 160 064 (J.F. EVERSOLE) * claim 1 *	1,4	
			TECHNICAL FIELDS SEARCHED (Int. Cl.)
			C 07 C 51/09 C 07 C 53/02
			CATEGORY OF CITED DOCUMENTS
			X: particularly relevant A: technological background O: non-written disclosure P: intermediate document T: theory or principle underlying the invention E: conflicting application D: document cited in the application L: citation for other reasons
<input checked="" type="checkbox"/> The present search report has been drawn up for all claims			&: member of the same patent family, corresponding document
Place of search Berlin		Date of completion of the search 29-08-1979	Examiner KNAACK

**This Page is Inserted by IFW Indexing and Scanning  
Operations and is not part of the Official Record**

**BEST AVAILABLE IMAGES**

Defective images within this document are accurate representations of the original documents submitted by the applicant.

Defects in the images include but are not limited to the items checked:

- ☐ BLACK BORDERS
- ☐ IMAGE CUT OFF AT TOP, BOTTOM OR SIDES
- ☐ FADED TEXT OR DRAWING
- ☒ BLURRED OR ILLEGIBLE TEXT OR DRAWING
- ☐ SKEWED/SLANTED IMAGES
- ☐ COLOR OR BLACK AND WHITE PHOTOGRAPHS
- ☐ GRAY SCALE DOCUMENTS
- ☒ LINES OR MARKS ON ORIGINAL DOCUMENT
- ☐ REFERENCE(S) OR EXHIBIT(S) SUBMITTED ARE POOR QUALITY
- ☐ OTHER: \_\_\_\_\_

**IMAGES ARE BEST AVAILABLE COPY.**

**As rescanning these documents will not correct the image problems checked, please do not report these problems to the IFW Image Problem Mailbox.**